SULFONATED ARYLSTEARIC ACIDS

Wetting Properties of the Sodium Salts

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Sulfonation of arylstearic acids derived from oleic acid takes place in the aromatic nucleus. Disodium sulfoarylstearates have penetrant properties and calcium stability equal to some commercial wetting agents. Penetrant properties are at a maximum at pH 4 to 6 and at a minimum in one per cent sodium hydroxide.

ARYLSTEARIC compounds derived from oleic acid are of value as addition agents to lubricants (*11*) and may be used as intermediates for further synthesis. A study of the nitro compounds is in progress, and the present report concerns the sulfonation products.

Since the previous publication (*10*) by two of the authors, further data have been obtained on the preparation of arylstearic acids and esters. The yield with and without fractionation under vacuum is recorded in Table I. The products are oils and distill between 200° and 300° C. at 0.1 to 0.5 mm., depending on the compound. Since the first report ethylbenzene, *sec*-amylbenzene, diethylbenzene, *p*-cymene, *m*-diisopropylbenzene, pseudocumene, tetrahydronaphthalene, and phenetole have been condensed with oleic acid by the Friedel and Crafts reaction.

Twitchell's reagent, for which the formula

$$CH_3(CH_2)_7\underset{\displaystyle ArSO_3H}{\underset{|}{C}}H(CH_2)_8CO_2H$$

is frequently written, has been considered the first synthetic wetting agent and the precursor of the Nekals (*2*, *5*, *6*, *9*). As prepared, however, by the sulfuric acid condensation of oleic acid and an aromatic compound, the product is a black oily mixture of several ingredients. It can be purified only by rather elaborate methods (*7*, *8*). Penetration properties and lime stability are relatively poor.

A sulfonaphthylstearic acid was prepared by Schlutius (*8*) by a Friedel and Crafts reaction, followed by sulfonation. It had fat-splitting properties and was apparently identical with the essential constituent of Twitchell's reagent. Wetting-agent properties were not investigated.

The simpler arylstearic acids of the benzene series can be obtained in about 50 per cent yield on vacuum distillation, and the yield on monosulfonation is about 75 per cent. The sodium sulfoarylstearates have penetrant and emulsifying properties, and the free acids are fat-splitting reagents.

The preparation and resistance to precipitation by calcium salts (calcium stability) of eight monosulfonated products are recorded in Table II. The disodium sulfoarylstearates can be used effectively in hard water and have about the same degree of calcium stability (400 to 700 p. p. m. calcium carbonate) as six of the thirteen commercial wetting agents listed in Table

The yield of the monosulfonated product is low when the aromatic reactant is highly alkylated. Thus the arylstearic acids derived from *sec*-amylbenzene, *m*-diisopropylbenzene, tetrahydronaphthalene, and pseudocumene, when sulfonated under the conditions of Table II, yield only about 30 per cent of the disodium sulfoarylstearate, and the bulk of the product is an insoluble black oil.

The presence of the sulfo group in the aromatic nucleus was established by oxidative degradation of disodium sulfophenylstearate with potassium permanganate. The product, isolated as the acid barium salt (*4*), was identified as the acid barium salt of *p*-sulfobenzoic acid. The melting point of the free anhydrous acid was 259–260° C. Found: per cent water of hydration, 9.02; calculated for $Ba(C_7H_5O_5S)_2$ +

TABLE I. YIELDS OBTAINED IN THE PREPARATION OF ARYLSTEARIC ACIDS AND ESTERS[a]

Compound	Yield, %: Crude	1 vacuum distn.	2 vacuum distns.
Phenylstearic acid	83	44	39
Tolylstearic acid	86	59	52
Ethylphenylstearic acid	87	53	47
Amylphenylstearic acid	76	37	27
Xylylstearic acid	89	63	53
Diethylphenylstearic acid	79	45	38
Cymylstearic acid	68	42	35
Diisopropylphenylstearic acid	69	46	39
Pseudocumylstearic acid	79	52	43
Tetrahydronaphthylstearic acid	95	49	..
Chlorophenylstearic acid	74	41	..
Ethoxyphenylstearic acid	88	48	42
Phenoxyphenylstearic acid	88	42	..
Xenylstearic acid	63	31	..
Ethyl tolylstearate	88	56	..
Methyl xylylstearate	91	63	..
Ethyl xylylstearate	82	56	..
Butyl xylylstearate	90	72	..
Methyl phenoxyphenylstearate	85	53	..

[a] Conditions: ratio ArH to oleic acid (or alkyl oleate), 6 to 1; ratio $AlCl_3$ to oleic acid (or alkyl oleate), 1.07 to 1. Temperature 80° C., time 4 hours. The reaction mass (in the case of the acids) was hydrolyzed in dilute hydrochloric acid, allowed to stand on the steam bath several hours, separated, and washed with hot water. Excess of ArH was recovered by steam distillation. Distillation was continued for 30 minutes with superheated steam. This left the oil virtually dry, and it was then distilled at about 0.1 to 0.5 mm. of mercury.

TABLE II. CONDITIONS OF PREPARATION, YIELD, SULFUR AND SODIUM CONTENTS, AND CALCIUM STABILITY OF DISODIUM SULFOARYLSTEARATES[a]

ArH[b]	Sulfonation Temp., ° C.	% Yield on Sulfonation[c]	Analysis: % S Found	% S Theory	% Na Found	% Na Theory	Ca Stability, P. P. M. $CaCO_3$[d]
Benzene	80	73	6.43	6.62	9.17	9.50	716
Toluene	80	76	6.24	6.43	9.20	9.23	577
Ethylbenzene	80	76	6.06	6.26	8.70	8.98	540
sec-Amylbenzene	60	26	5.89	5.78	8.12	8.30	405
m-Xylene	80	75	6.36	6.26	8.91	8.98	516
p-Cymene	60	52	5.76	5.93	8.13	8.51	447
m-Diisopropylbenzene	70	22	5.70	5.64	7.97	8.09	422
Phenetole	50	80	6.28	6.07	8.71	8.71	668

[a] Conditions: mole ratio 95% H_2SO_4 to arylstearic acid, 8 to 1. The arylstearic acid was added gradually, with continuous agitation, to H_2SO_4 and the indicated temperature then maintained for 1 hour. The monosulfonated product was isolated on the basis of insolubility in dilute H_2SO_4, solubility in ether, water extraction of the ether solution, evaporation of the neutralized (NaOH) aqueous solution to dryness, extraction with alcohol, clarification of the alcohol solution, and evaporation to dryness.
[b] ArH designates the aromatic reactant yielding the disodium sulfoarylstearate.
[c] Isolated as the disodium salt.
[d] Determined by a modified Hart method (*12*).

TABLE III. PENETRANT PROPERTIES OF DISODIUM SULFOARYLSTEARATES

ArH	Sinking Time, Seconds[a]								
	Distd. water soln. (pH 7.4–7.8)	Slightly acid soln. (H_2SO_4)	H_2SO_4 1 %	H_2SO_4 2 %	H_2SO_4 5 %	NaOH 1 %	NaOH 5 %	NaOH 15 %	NaOH 20 %
Benzene	30	10.2 (pH 3.6)	15	16.4	28.4	>1800	>1800	188	189
Toluene	19.1	9.7 (pH 6.1)	14.9	18.3	35	1484	830	187	172
Ethylbenzene	17.3	10.6 (pH 6.6)	16	19.7	36	>1800	509	92	183
sec-Amylbenzene	13.6	14.1 (pH 6.1)	23.7	24.4	36	426	112	84	161
m-Xylene	14.7	8.3 (pH 5.9)	19.9	20	30	777	218	74	300
p-Cymene	16.7	14.6 (pH 4.2)	25.4	26.8	39	798	365	150	209
m-Diisopropylbenzene	17.0	13.2 (pH 5.7)	20.5	25.8	44	428	180	119	177
Phenetole	10.1	6.3 (pH 6.3)	10.9	17.8	26.2	530	438	129	230

[a] Draves-Clarkson test on 0.2 % solutions.

$3H_3O$: per cent H_2O = 9.11. Found: per cent barium, 23.05; calculated for $Ba(C_7H_5O_5S)_2 + 3H_2O$: per cent Ba, 23.14.

When sulfonated under similar conditions, esters such as methyl xylylstearate produce a mixture of methyl sodium sulfoxylylstearate and disodium sulfoxylylstearate. Since these products did not represent an advantage in the sinking time tests or in resistance to precipitation by calcium salts, the study of the sulfonation of esters was discontinued.

The main product in the sulfonation of phenoxyphenylstearic and xenylstearic acids under the conditions of Table II is the disulfo compound. Conditions can be adjusted so that either the mono or the disulfo compound is isolated. The monosulfo compounds have superior wetting power, but the calcium salts of the disulfo compounds are very soluble.

Undecylenic acid can be used in place of oleic in the Friedel and Crafts reaction with an aromatic compound (*3*) and the arylundecylic acid may then be sulfonated. The products have wetting power and resistance to precipitation by calcium salts to about the same degree as those obtained from arylstearic acids.

and 20 per cent sodium hydroxide. Wetting time increases as the acidity increases from 1 to 2 to 5 per cent sulfuric acid.

The wetting efficiency is poor in 1 per cent sodium hydroxide. As the concentration of sodium hydroxide increases from 1 to 5 to 15 per cent, the sinking time decreases. Beyond this point sinking time increases or remains virtually the same.

Disodium sulfoethoxyphenylstearate and disodium sulfoxylylstearate were selected as having the best properties from the point of view of overall yield and wetting efficiency. The influence of concentration on sinking time is listed for these two compounds in Table V.

The surface tension of a 1 per cent solution and the interfacial tension between solution and a highly refined mineral

TABLE IV. PENETRANT PROPERTIES OF COMMERCIAL WETTING AGENTS

Type of Product	% Concentration[a]	Sinking Time, Sec. Distd. water	5% NaOH	5% H_2SO_4
$ROOCCH_2$ $ROOCCHSO_3Na$	0.04	8.3	>1800	25.2
R_2CHOSO_3Na				
Product 1	0.8	587	84	472
Product 2	0.2	5.4	660	>1800
Product 3	0.2	51	41	14.6
RCH_2OSO_3Na				
Product 1	0.2	74	158	108
Product 2	0.2	10.0	30	10.0
Product 3	0.2	21.8	110	21.5
$RCON(CH_3)C_2H_4SO_3Na$	0.2	50	93	93
Alkylarylsulfonate				
Product 1	0.2	10.5	19.5	10.6
Product 2	0.2	31	>1800	42
Product 3	0.2	56	18.4	10.3
Sulfonated aromatic ether alcohol	0.2	85	438	135
Highly sulfonated oil	0.2	160	104	...

[a] For example, a concentration of 0.2% means a solution containing 2 grams of the commercial product per liter.

TABLE V. INFLUENCE OF CONCENTRATION

Disodium Arylstearate	0.05% Concn.		0.1% Concn.		0.2% Concn.		0.4% Concn.	
	Distd. water	Slightly acid soln.	Distd. water	Slightly acid soln.	Distd. water	Slightly acid soln.	Distd. water	Slightly acid soln.
Sulfoxylyl	44	40 (pH 5.3)	22.5	17.5 (pH 5.9)	14.7	8.3 (pH 5.9)	10.6	6.4 (pH 6.5)
Sulfoethoxyphenyl	34	31 (pH 5.3)	20.5	17.4 (pH 6.4)	10.1	6.3 (pH 6.3)	6.6	4.4 (pH 6.6)

The penetrant properties of the disodium sulfoarylstearates were determined by the Draves-Clarkson sinking time test (*1*). These values are recorded in Table III and may be compared with the data of Table IV obtained with samples of commercial wetting agents.

The disodium sulfoarylstearates were tested for their stability to boiling alkali and acid. The wetting efficiency of a 0.2 per cent solution of disodium sulfoxylylstearate in 15 per cent sodium hydroxide remained unchanged after refluxing for 2 hours. However, when the same treatment was given to a 0.2 per cent solution in 2 per cent sulfuric acid, the sinking time increased from 20 to 42 seconds. This degree of stability represents an advantage over wetting agents with an ester linkage. Some samples of the ester types of commercial wetting agents lost all penetrant properties when they were heated in acid solution under the same conditions.

All of the preparations of the disodium sulfoarylstearates were slightly alkaline in 0.2 per cent solution (pH 7.4 to 7.8), and it was found that the penetrant properties were quite sensitive to acidity and alkalinity. When a 0.2 per cent solution was made slightly acid with sulfuric acid, the sinking time in most cases decreased notably. Apparently the optimum pH, as far as penetrancy is concerned, is near the range 4 to 6. Wetting time measurements were made on these compounds in 1, 2, and 5 per cent sulfuric acid and in 1, 5, 15,

oil were measured. At 25° C. the values are as follows, in dynes per cm.: disodium sulfoxylylstearate: surface tension 41.7, interfacial tension 10.0; disodium sulfoethoxyphenylstearate: surface tension 40.0, interfacial tension 17.0.